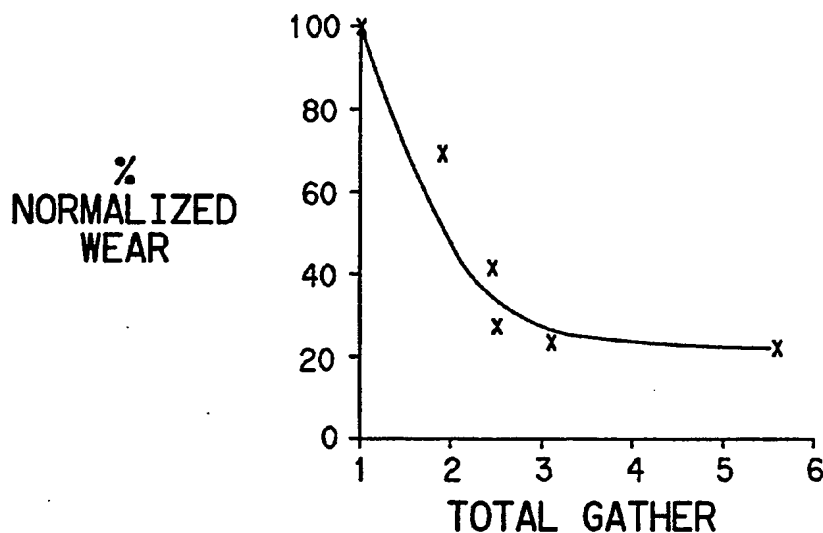




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(54) Title: ABRASION-RESISTANT RESIN IMPREGNATED NONWOVEN FABRIC



(57) Abstract

Abrasion-resistant nonwoven fabrics are prepared by contracting the area of a lightweight fibrous layer to less than half its original area so that groups of fibers buckle and form inverted U-shaped loops that project from the plane of the layer and then resin impregnating the fabric to immobilize the loops and stabilize the dimensions of the contracted fibrous layer.

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TITLE

Abrasion-resistant Resin-impregnated Nonwoven Fabric

BACKGROUND OF THE INVENTION

Field of the Invention

5 This invention relates to a process for making a resin-impregnated nonwoven fabric. More particularly, the invention concerns such a process wherein a starting nonwoven fibrous layer is significantly contracted in area causing groups of its fibers to buckle out of plane, the buckled groups of fibers are immobilized in their buckled position, and the fabric is dimensionally stabilized. Novel products
10 of the process have unexpectedly high abrasion resistance in comparison to known contracted nonwovens in which the buckled fibers are not immobilized and the fabric is not stabilized.

Description of the Prior Art

Processes are known wherein a nonwoven fibrous layer is buckled, shirred,
15 gathered or puckered so that the final area of the fibrous layer is much contracted in comparison to the original area of the layer. For example, such processes are disclosed by Bassett United States Patent 3,468,748, Wideman U.S. 4,606,964, and Zafiroglu U.S. 4,773,238. The contraction can cause groups of fibers of the nonwoven fibrous layer to buckle out of plane and to form generally "U-shaped"
20 loops projecting from the plane of the layer. Further treatments of such contracted layers also are known. For example, Hansen U.S. 3,575,782, discloses making a shirred elastic fabric by sealing partially extended, spaced apart, aligned elastic yarns between thin porous nonwoven fibrous webs and then allowing the yarns to contract, the sealing agent being a soft flexible polymeric binder (e.g., rubber
25 latex). Although useful in some applications, the impregnated shirred fabrics of Hansen often are excessively stretchable and insufficiently resistant to abrasion for satisfactory use in other applications, such as athletic shoe parts, luggage surface layers, work clothes pockets, wear surfaces of automotive timing belts, marine abrasion pads and the like.

30 An aim of this invention is to enhance the utility of resin-impregnated nonwoven fabrics by providing such fabrics with high abrasion resistance and low stretchability.

SUMMARY OF THE INVENTION

The present invention provides a process comprising the steps of:
35 contracting a nonwoven fibrous layer in area to an area that is no greater than one-half its original non-contracted area of the layer and causing groups of fibers of the nonwoven fibrous layer to buckle out of the plane of the layer and form inverted U-shaped loops projecting in a direction generally perpendicular to the plane of the

layer, immobilizing the buckled groups of fibers, and stabilizing the dimensions of the contracted fibrous layer. Preferably, the fibrous layer area is contracted to less than one-third the original area. In one embodiment of the process, a contractible element or array of contractible elements is intermittently attached to the nonwoven
5 fibrous layer, the intermittently attached element or array of elements is contracted to cause an accompanying contraction of the nonwoven fibrous layer and the buckling of the groups of fibers. Preferably, the buckled groups of fibers are immobilized by impregnating the fibrous layer with a resin and then curing and/or drying the resin. Preferably, the dimensions of the contracted layer are stabilized
10 simultaneously with the immobilization of the buckled groups of fibers during the resin-impregnation-and-curing step. Typically, the dry resin preferably amounts to in the range of 10 to 90% of the total weight of the impregnated layer, preferably 25 to 75%. The layer of impregnated and immobilized projecting loops form an abrasion-resistant surface. Alternatively, the dimensions of the contracted fibrous
15 layer can be stabilized by attaching a substantially non-stretchable element or array of non-stretchable elements to the back surface (i.e., the surface opposite to the abrasion-resistant surface) of the contracted, buckled, fibrous layer.

The present invention also provides a novel, resin-impregnated nonwoven fabric which comprises a fibrous layer from which groups of fibers are buckled out
20 of plane. The buckled groups of fibers have an average spacing in the range of 0.5 to 3 mm, preferably 1 to 2 mm. The fabric is stretchable (as defined hereinafter) in any linear direction by no more than 50%, preferably by no more than 25% and most preferably by no more than 5%. Contracted, resin-impregnated fabrics weigh in the range of 150 to 1200 g/m², of which 10 to 90 weight percent is composed of
25 fibers, and the groups of buckled fibers have an average loopiness (i.e., height-to-base ratio measured as described hereinafter) of at least 0.5, most preferably in the range of 0.7 to 1.5.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be better understood by referring to the attached
30 drawings wherein Figures 1-4 present graphs of abrasion resistance as functions of total gather of the contracted, resin-impregnated fabrics of Examples 1-4, respectively, and Figures 5 and 6 represent magnified schematic cross-sections of groups of buckled fibers formed into projecting U-shaped loops **10**, with height **H** and base **B**, indicated thereon. Figure 5, in which contractable elements **20** are
35 stitching yarns, is representative of Examples 1, 2, 4 and 5, and Figure 6, in which the contractible element **30** is a thin elastic sheet, is representative of Example 3.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The invention is further illustrated by the following description of preferred embodiments. These are included for the purposes of illustration and are not intended to limit the scope of the invention, which is defined by the appended claims.

As noted above, in the first step in the process of the present invention, a nonwoven fibrous layer is contracted to an area that is no greater than one-half its original planar area.

The starting nonwoven fibrous layer that is to be contracted and buckled in accordance with the invention typically is a thin, supple, substantially nonbonded web of staple fibers, continuous filaments, plexifilamentary strands or the like. The term "fibers" is used collectively herein to include each of these fibrous materials. The fibers may be natural fibers or may be formed from synthetic organic polymers. Fibers of less than about 5 dtex and of at least 5-mm length are preferred. Preferred starting layers are capable of buckling, as shown in the examples below, over relatively short intervals (e.g., 1-mm). A suitable starting layer typically weighs in the range of 15 to 100 grams per square meter, preferably less than 60 g/m². Suitable materials for the starting nonwoven layers include carded webs, air-laid webs, wet-laid webs, spunlaced fabrics, spunbonded sheets, and the like. Generally, thick lofty webs, felted webs, adhesively or thermally bonded webs, or the like are not suited for use as the starting fibrous layer; such materials usually are difficult to buckle over short intervals.

The contraction and buckling of the fibrous layer can be accomplished in any of several known ways. In one method, a contractible element or an array of contractible elements is intermittently attached to the fibrous layer. Then, the element or array of elements is caused to contract so that the area of the fibrous layer is decreased significantly and groups of fibers buckle out of the plane of the layer. Before the contractible elements are attached, additional gathering or contraction can be imparted to the fibrous starting layer, by over-feeding the layer to the apparatus being employed to attach the contractible elements.

Many types of contractible elements are suitable for use in the invention. For example, the nonwoven fibrous layer can be stitch-bonded with elastic yarns under tension. Textured stretch yarns, covered or bare spandex yarns, and the like are suitable yarns for the stitching. After the stitching, the tension can be released from the stitching thread to cause the desired contraction and buckling of the fibrous layer. Instead of stitching, warps or cross warps of extended elastic elements can be intermittently attached to the fibrous layer by hydraulic entanglement, adhesive or thermal point bonding, or the like. Thereafter, tension on the extended elements is released to cause layer contraction and buckling.

Other types of contractible elements, which shrink on being treated with heat, moisture, chemicals or the like can be attached intermittently to the fibrous layer without initial tension or extension in the elements. After attachment, the contraction of the contractible elements can be activated by appropriate treatment.

- 5 Still another way of accomplishing the contraction and buckling of the fibrous layer involves intermittently attaching the fibrous layer to a stretchable substrate that necks-in in a direction perpendicular to the direction in which the substrate is pulled. For example, certain substrates, when stretched by 15% in one direction, can automatically experience substantially irreversible contraction (i.e., neck in) in
10 a direction perpendicular to the stretch by an amount that is two or three times the percentage stretch. Thus, appropriate intermittent attachment of a fibrous layer to the stretchable substrate before the stretching and necking-in operation, and then applying the stretching forces to the combined layer and substrate, can significantly decrease the area of the fibrous layer and cause buckling of groups of fibers as
15 required by the process of the invention.

When performing the contracting step in accordance with the process of the invention, the area of the fibrous web is decreased to an area that typically is no greater than one-half, preferably no greater than one-third, of the original area of the non-contracted layer.

- 20 Several of the above-described methods of attaching contractible elements to the fibrous layer and then contracting the elements and the layer are illustrated in the Examples below.

- To achieve high resistance to abrasion in the resin-impregnated fabrics of the present invention, the buckled groups of fibers of the contracted fibrous layer
25 generally extend in a direction perpendicular to the plane of the nonwoven fibrous web and are immobilized in that position. The buckled groups of fibers are packed closely together as a result of the contraction of the layer. Dried and/or cured resin prevents the buckled groups of fibers from moving from side to side or collapsing into the layer when the surface of the layer is abraded or rubbed.

- 30 Various types of resins are suitable for immobilizing the fiber bundles. Particularly useful are various resins of polyurethane, epoxy, rubber and the like. The resin may be applied in any of several conventional ways. For example, the fibrous layer may be resin-impregnated by dipping, spraying, calendering, applying with a doctor knife, or other such techniques. The resin may be applied from a
35 solution, slurry or by melting a layer of the resin and forcing it into the contracted fibrous layer. The resin can be introduced as adhesive particles or as binder fibers that are activated by heat. In most instances, the resin or binder can be introduced into the fibrous layer before, during or after contraction. However, care must be taken, when introducing the resin or binder into the layer before contraction, not to

immobilize the fibers before the contraction or gathering of the layer is effected. Accordingly, it is preferred to apply the resin, after the fibrous layer has been subjected to the desired contraction step and then to allow the resin to dry, harden and/or cure.

5 Figure 5 and 6 schematically represent (in magnification) typical immobilized loops formed by the buckled groups of fibers of the contracted or gathered fibrous layer, with height H and base B dimensions designated on the figures. Typically, the loops of buckled groups of fibers have an average spacing in the range of 0.5 to 3 mm, preferably 1 to 2 mm. Various practical methods are
10 available to determine the H and B dimensions of the loops, as described below in the paragraphs on test methods.

 The resin-impregnated contracted fibrous layer of the invention typically has a stretchability in any linear direction of no more than 50%, preferably no more than 25% and most preferably by no more than 5%. As used herein, a fabric is
15 deemed to be "substantially non-stretchable" if the fabric has a stretchability of less than 5%. Stretchability is an inverse measure of the dimensional stability of the fabric.

 Stretchability of the fabric can be controlled in several ways. Most conveniently, the stretchability is limited to very low values by the use of a hard
20 resin that stabilizes the dimensions of the fabric while it simultaneously immobilizes the buckled fiber loops. The degree of fabric dimensional stability obtained by this method is also indicative of the degree of buckled fiber loop immobilization. Very low levels of fabric stretchability (i.e., high dimensional stability) achieved by resin impregnation are always accompanied the high levels
25 of buckled fiber loop immobilization. Fabric stability can also be achieved by the attachment of strong, substantially non-stretchable strips, films, sheets, webs, cross-warps and the like to the back surface of the abrasion-resistant layer. The attachment may be by any convenient means, such as gluing, thermal bonding and the like.

30 Fabrics contracted in accordance with the invention are suitable for molding into shaped articles, such as tires, timing belts, gloves, shoes, luggage, edge and corner protectors, and the like. Conventional means for shaping the fabric are employed. For example, the resin-impregnated contracted fabric can be placed in a mold before the resin is still has hardened, and then allowed to set while in the
35 mold.

 The following methods and procedures are used to measure various characteristics of the resin-impregnated fabrics of the invention.

 The height H and the base B of the U-shaped loops of buckled groups of fibers are determined from magnified (e.g., 15-20X) photomicrographs of cross-

sections of the loops taken through the loops in a plane perpendicular to the plane of the fibrous layer. The data are then used to calculate an "H/B ratio". A low magnification microscope with strong top and/or back lighting on the sample permit direct measurement of the H and B. Usually the average loop height H is
5 equal to the thickness of the contracted fibrous layer. As used herein, "loop spacing" is synonymous with the loop base B, (i.e., the distance between the legs of the inverted "U" that formed the loop of buckled fibers). Alternatively, the average loop height H is sometimes easier to measure directly with a "touch" micrometer having a 1/4-inch (0.64-cm) diameter flat cylindrical probe which applies a 10-
10 gram load to the contacted surface. A digital micrometer, model APB-1D, manufactured by Mitutoyo of Japan is suitable for measuring these thicknesses or heights.

Stretchability is determined by: (a) cutting a sample measuring 2-inches (5.1-cm) wide by 4-inches (10.2-cm) long sample from the layer; (b) marking a
15 standard length, L_o , parallel to the long dimension of the sample; (c) suspending a 10-pound (454-gram) weight from sample for 2 minutes; (d) with the weight still suspended from the sample, re-measuring the "standard length", the re-measured length being designated L_f ; and (e) determining the stretchability as %S by the formula, $\%S = 100 (L_f - L_o)/L_o$.

20 To determine the abrasion resistance of samples a Wyzenbeek "Precision Wear Test Meter", manufactured by J. K. Technologies Inc. of Kankakee, Illinois, is employed with an 80-grit emery cloth wrapped around the oscillating drum of the tester. The drum is oscillated back and forth across the face of the sample at 90 cycles per minute under a load of six pounds (2.7 Kg). The test is conducted in
25 accordance with the general procedures of ASTM D 4157-82. The thickness of the sample is measured with the aforementioned micrometer before and after a given number of abrasion cycles to determine the wear in mm of thickness lost per 1,000 cycles.

The unit weight of a fabric or fibrous layer is measured according to ASTM
30 Method D 3776-79. The density of the resin-impregnated fabric is determined from its unit weight and its thickness, measured as described above.

Over-feed ratio, contraction ratio and total gather are parameters reported herein which measures of how much an initial fibrous layer contracts or gathers as a result of the operations to which the layer is subjected. The over-feed ratio is
35 defined as the ratio of the initial area of the starting fibrous layer to the area of the layer immediately up-stream of a first processing step (e.g., a stitchbonding step). Over-feed causes gathering or compression of the layer in the direction in which it is being fed to the operation. The contraction ratio is a measure of the amount of further contraction the layer undergoes as a result of the specific operation to which

it is subjected (e.g., stitchbonding, release of tension from yarns to which the fibrous layer was intermittently attached). The contraction ratio is defined as the area of the fibrous layer as it enters the specific operation divided by the area of the fibrous layer as it leaves the specific operation. The total gather is defined as the product of the over-feed and contraction ratios. The fraction of original area is the reciprocal of the total gather and is equivalent to the ratio of the final area of the fibrous layer to the initial area of the starting fibrous layer.

EXAMPLES

The following Examples illustrate the invention and compare samples made in accordance with the invention to samples that are outside the scope of the invention. The examples also illustrate how the abrasion resistance of resin-impregnated samples is affected by changes in over-all gather, loop height-to-base ratio, fiber immobilization and fabric stabilization. In the Examples, all percentages, unless stated otherwise, are based on the total weight of the resin-impregnated contracted fibrous layer. A summary table of data accompanies each example and records the unit weight, composition, thickness, fiber concentration in the impregnated fibrous layer, loop spacing, loop height-to-base ratio, various gather parameters, stretchability and the abrasion resistance of each sample. Samples of the invention are designated with Arabic numerals; comparison samples, with upper case letters. The reported results are believed to be fully representative of the invention, but do not constitute all the tests involving the indicated fibrous layers and resins.

Example 1

This example illustrates the manufacture of resin-impregnated contracted fibrous samples of the invention, in which the contraction of the fibrous starting layer is accomplished by several different techniques, including: over-feeding (Samples 1, 2 and B); stitchbonding with elastomeric yarn under tension and then heat setting to achieve different amounts of contraction (Samples 1, 2, A and B); stretching a neckable web to which the fibrous layer had been attached (Sample 3); and intermittently attaching tensioned elastic yarns to a fibrous layer and releasing the tension (Sample 4). The contracted-and- resin-impregnated samples of the invention are compared to similarly prepared samples outside the invention.

For each of the samples prepared by the procedures of this example, the starting fibrous layer was made of Kevlar® mid staple fibers of 7/8-inch (2.2-cm) length and 1.5 denier (1.7 dtex). Kevlar® is a fiber is a product manufactured and sold by E. I. du Pont de Nemours and Company of Wilmington, Delaware.

The starting fibrous layer of Samples 1 and 2 of the invention and comparison Samples A and B consists of one or two layers of lightweight Type Z-11 Sontara® spunlaced fabric of Kevlar® aramid staple fiber (made and sold by E. I.

du Pont de Nemours and Company). The starting fibrous layer was stitchbonded with 280-den (311-dtex) yarn of 70-den (78-dtex) Lycra[®] spandex covered with textured polyester yarn. A Liba warp-knitting machine was employed with one bar fully threaded at 12 gauge (4.8 needles per cm) and forming 14 courses per inch (5.5 per cm). A 1-0,2-3 repeating stitch pattern was employed. (Conventional warp knitting nomenclature is used herein to describe the stitch pattern.) Each sample was then heat set at 380°F (193°C) for 2 minutes on a tenter frame with different amounts of longitudinal and transverse stretch.

The starting fibrous layer of Sample 3 was a 0.85-oz/yd² (29-g/m²) air-laid web of the Kevlar[®] aramid fibers. The web was attached to a highly entangled layer of 0.7-oz/yd² (24-g/m²) Style 8417 Sontara[®] spunlaced fabric of polyester fibers. The attachment was made by conventional hydraulic entanglement techniques. The polyester spunlaced fabric with the air-laid aramid-fiber web atop it were supported on a 24-mesh, 21%-open-area screen while being passed at 10 yards per minute (9.1 m/min) under columnar streams of water which emerged from a row of 0.007-inch (0.18-mm) diameter orifices. The row of orifices were located about 1 inch (2.5 cm) above the screen and extended transverse of length of the moving assembly. The orifices were spaced in the row at 10 per inch (3.9/cm) and were supplied with water at a pressure of 500 psig (3450 kPa). The hydraulic jet treatment caused lanes of attachment between the yarns and the web to be formed, which were spaced at a frequency of 10 per inch (3.9/cm). The thusly assembled web and spunlaced fabric was stretched in the longitudinal direction by 15%. The longitudinal stretch was accompanied by a contraction in the transverse direction (i.e., necking-in) that resulted in a decrease in area to 40% of the original not-stretched and not necked-in area. The contraction caused groups of fibers to form inverted U-shaped loops which projected from the plane of the assembly. The loops in the contracted fabric were spaced along the transverse direction with a frequency of 28 loops per inch (11/cm).

Sample 4 was prepared by placing a layer of aramid fiber web over a tensioned 12-gauge warp (i.e., 12/inch or 4.7/cm) of 140-den (154-dtex) Lycra[®] spandex which was wrapped with 70-den (78-dtex) polyester yarn and then subjecting the warp and web to a hydraulic entanglement treatment. Each yarn in the tensioned warp had about a 30% residual stretch (i.e., could have been stretched an additional 30%) with the polyester yarn wrapping extended to about 8 turns per inch (3.1/cm). The hydraulic treatment consisted of passing the assembled web and warp, while supported on a 24-mesh, 21%-open-area screen, at 10 yds/min (9.1 m/min) under columnar jets of water emerging from a row of 0.005-inch (0.13-mm) diameter orifices located about 1 inch (2.5 cm) above the assembly. The row of orifices were positioned transverse to the array of yarns and numbered 40 per

inch (15.7/cm). The assembly was subjected to the hydraulic jets in three passes under the orifices. The pressure of the water supplied to the orifices was 200, 1000 and 1800 psig (1380, 6890 and 12,400 kPa) during the first, second and third passes, respectively. After the hydraulic jet treatment, tension was released from the yarns of the warp. The tension release caused contraction to about 1/3 of the original area of the starting aramid fiber web and gathering of groups of aramid fibers into inverted U-shaped loops.

Control sample C consisted of three superimposed flat layers of Type Z-11 Sontaraâ made of Kevlarâ aramid staple fibers.

Each of the above-described samples were impregnated with a polyurethane resin. The resin was applied from a solution of "ZAR" clear polyurethane finish (manufactured and sold by United Gilsonite Laboratories of Scranton, Pennsylvania) by dipping the sample into the finish, allowing the excess to drip from the sample, and then drying the sample in air for 48 hours at 25°C and 40% relative humidity. Each of the samples were then subjected to abrasion testing. Table I summarizes the test results along with various characteristics of the dried, resin-impregnated samples. The results of the abrasion tests are presented graphically in Figure 1.

The Table and Figure clearly demonstrate the unexpectedly large advantages in abrasion resistance possessed by Samples 1-4, which were made in accordance with the invention, over the comparison Samples A, B and C, which were outside the invention. Note that when samples had a total gather of less than 2.0 and/or a loop H/B ratio of less than 0.5, the abrasion resistance of the resin-impregnated fabric was very much lower than the abrasion resistance of the fabrics of the invention. Samples 1-4 of the invention were about 240 to 475% more resistant to abrasion than comparison samples that had not been contracted. Note also that the abrasion resistance appears to be largely unaffected by the concentration of fiber in the impregnated layer, within the range of fiber concentrations tested.

TABLE I

Sample Identification	A	B	C	1	2	3	4
Product unit weight, g/m ²							
Fibrous Layer	110	78	119	212	220	70	180
Total	1000	600	540	1010	710	260	410
Weight percent							
Fibrous Layer	11	13	22	21	31	27	44
Contractible elements	2	6	0	5	12	33	4
Resin	87	81	78	74	57	40	52
Fiber concentration, g/cm ³	0.08	0.08	0.14	0.13	0.17	0.11	0.11
Total thickness, mm	1.2	0.9	0.8	1.5	1.2	0.6	1.5
Loop base, B, mm	2.8	2.3	Na ⁺	1.9	1.4	1.0	1.3
Loop H/B ratio	0.43	0.37	Na	0.80	0.86	0.60	1.20
Gather							
Over-feed ratio	1.0	1.36	1.0	1.30	1.31	Na	Na
Contraction ratio	1.0	1.4	1.0	2.0	4.2	2.5	3.1
Total gather	1.0	1.9	1.0	2.6	5.5	2.5	3.1
Fraction of original area	1.0	0.53	1.0	0.38	0.18	0.40	0.32
Stretchability, %	0	0	0	0	0	0	0
Abrasion resistance							
Test duration, 10 ³ cycles	2.5	3.0	6.0	7.0	12.0	8.0	9.0
Wear, mm/10 ³ cycles	0.12	0.08	0.12	0.05	0.025	0.032	0.030
% normalized wear*	100	69	100	42	21	27	25

Notes: * % normalized wear is normalized to Sample C.

+ "Na" means not applicable.

Example 2

This example illustrates the fabrication of resin-impregnated, contracted nonwoven fabrics of the invention, Samples 5 and 6, in which the starting fibrous layer is a sheet of flash-spun plexifilamentary film-fibril polyethylene strands and compares their abrasion resistance with similarly prepared comparison Samples D and E which were not subjected to the desired amount of gather. Whereas Samples 5 and 6 were subjected to a total gather of 2.7 and 5.7 respectively, comparison Samples D and E, which are outside the invention, were subjected respectively to no contraction at all (Sample D) or to a total gather of only 1.76 (Sample E). As a result of the appropriate contraction, the Samples of the invention were about 20 to

100 times as resistant to abrasion as were the comparison samples. Table II, below, summarizes detailed characteristics of the samples. Figure 2 graphically displays the advantages in abrasion resistance having resin-impregnated fabrics of the invention prepared with total gathers of at least 2.0. Further details on the
5 fabrication of the samples are given in the following paragraphs.

The starting fibrous layer of each of the samples of this example was a lightweight, non-bonded sheet of flash-spun plexifilamentary film-fibril polyethylene strands which had been treated with hydraulic jets in accordance with the general procedures of Simpson et al, U. S. Patent 5,023,130. The hydraulic jet
10 treatment consisted of supporting the non-bonded sheet on a 24-mesh, 21%-open-area screen, and passing the sheet one time at 10 yds/min (9.1 m/min) under columnar jets of water emerging from a row of 0.005-inch (0.13-mm) diameter orifices, spaced at 40 orifices per inch (15.7/cm) in the row, the row of orifices being positioned about 1 inch (2.5 cm) above the screen and transverse to the
15 direction of movement of the sheet. Water was supplied to the orifices at a pressure of 500 psig (3450 kPa). Such starting fibrous layers are available commercially as Typroâ from E. I. du Pont de Nemours and Company. One or two layers of 1.3 oz/yd² (44 g/m²) commercial Typroâ was used for the samples of this example.

20 The hydraulic-jet-treated fibrous layers of Typroâ sheet of Samples 5, 6 and comparison E were contracted by stitchbonding with a "Liba" machine with the stitching yarns under tension and then releasing the tension from the yarns. Comparison sample D, was not stitched or contracted. For Samples 5 and 6 of the invention, the stitching yarn was a 140-den (154-dtex) Lycraâ spandex wrapped
25 with 70-den (78-dtex) polyester yarn and one fully threaded 12-gauge bar formed 1-0,1-2 stitches, 14 courses per inch (5.5/cm). For comparison Sample E, the stitching thread was a 70-den (78-dtex) textured nylon yarn and one fully threaded 12-gauge bar formed 1-0, 1-2 stitches, 9 courses per inch (3.5/cm). All samples were impregnated with a polyurethane resin by the same manner as in Example 1,
30 except that the polyurethane resin employed in this Example, when dry is much softer than the polyurethane resin of Example 1. The dry resin of Example 2, had a Shore A durometer hardness of about 53.

Further details of the samples and their performance are given in the following table.

TABLE II

Sample Identification	<u>D</u>	<u>E</u>	<u>5</u>	<u>6</u>
Product unit weight, g/m ²				
Fibrous Layer	44	82	260	272
Total	132	214	1075	1105
Weight percent				
Fibrous Layer	33	38	24	25
Contractible elements	0	10	7	10
Resin	67	52	69	65
Fiber concentration, g/cm ³	0.24	0.36	0.20	0.25
Total thickness, mm	0.18	0.23	1.32	1.07
Loop base, B, mm	Na	2.64	1.47	1.37
Loop H/B ratio	Na	0.09	0.89	0.78
Gather				
Over-feed ratio	Na	1.0	1.0	1.37
Contraction ratio	1.0	1.76	2.74	4.17
Total gather	1.0	1.76	2.74	5.7
Fraction of original area	1.0	0.57	0.36	0.17
Stretchability, %	0	0	0	0
Abrasion resistance				
Test duration, 10 ³ cycles	0.12	0.14	20	20
Wear, mm/10 ³ cycles	0.60	0.45	0.024	0.006
% normalized wear*	100	75	4	1

Notes: * % normalized wear is normalized to Sample C.

+ "Na" means not applicable.

Example 3

This example illustrates the effect of total gather on abrasion resistance with a commercial nonwoven material which is sold by Kimberly-Clark Corporation of Neenah, Wisconsin, and is referred to as "KC stretchbonded composite (B-16, SBL-13)". This material has inverted U-shaped loops on each of its two surfaces, as shown schematically in Figure 6. In this example, Sample 7 of the invention is shown to be 3 to 5 times as abrasion resistant as any of four comparison Samples F, G, H or I. Sample 7 has a total gather of 2.8 and a loop H/B ratio of 0.63, as compared to the comparison samples which have gathers in the range of 1 to 1.8 and loop ratios in the range of 0.11 to 0.32.

The KC stretchbonded composite which is starting fibrous layer for each of the samples of this example, has a very thin elastic layer that is located mid-plane between two spunbonded sheets of polypropylene fibers. The sheets apparently

- were thermally spot-bonded to the elastic layer while the elastic layer was under tension. Thereafter, the layer apparently was allowed to relax and gather by what appears to have been a factor of 2.8 in the longitudinal direction. To test the effects of total gather on the abrasion resistance of this material, polyurethane resin of
- 5 Example 1 was applied in the same manner as in Example 1 to samples of KC stretchbonded composite that were fully relaxed or stretched by different amounts to form Sample 7 (fully relaxed, total gather = 2.8) and comparison Samples F, G, H and I (with total gathers of 1.0, 1.1, 1.4 and 1.8, respectively). Further details of samples and their abrasion-test performance are given in Table III. Abrasion
- 10 performance is plotted in Figure 3, as a function of total gather.

TABLE III

Sample Identification	F	G	H	I	Z
Unit weight, g/m ²					
Fibrous two layers	22	24	30	39	60
Contractible layer	33	37	45	59	89
Total	614	678	885	925	1230
Weight Percent					
Fibrous two layers	3.6	3.5	3.4	4.2	4.9
Contractible layer	5.4	5.6	5.1	6.4	7.2
Resin	91.1	91.9	91.5	89.2	87.9
Fiber concentration, g/m ²	0.08	0.08	0.08	0.09	0.11
Total thickness, mm	0.28	0.29	0.38	0.45	0.57
Loop base, B, mm	2.5	2.3	1.8	1.4	0.9
Loop H/B ratio	0.11	0.12	0.21	0.32	0.63
Gather					
Total Gather	1.0	1.1	1.4	1.8	2.8
Fraction of original area	1.0	0.91	0.71	0.56	0.36
Stretchability, %	0	0	0	0	0
Abrasion resistance					
Test duration, 10 ³ cycles	1.1	1.1	0.5	0.7	1.1
Wear, mm/10 ³ cycles	0.46	0.32	0.30	0.31	0.09
% normalized wear*	100	70	65	67	20

Note: % normalized wear is normalized to Sample F.

Example 4

- A series of resin-impregnated, stitchbonded contracted samples was made by the procedures as were used in Example 1 for Samples 1, 2, A, B and C, and
- 15 with the same materials except that natural rubber RSS #1, manufacturing code 220-B40 was substituted for the polyurethane resin used in Example 1 to impregnate the fibrous layer of Kevlar® fibers. The same kinds of improvement in

abrasion resistance with increasing total gather as were shown in Example 1 are also demonstrated in this example. Sample details and abrasion test results are summarized in Table IV. Figure 4 displays the abrasion results graphically.

TABLE IV

Sample Identification	J	K	L	8	9
Product unit weight, g/m ²					
Fibrous Layer	122	108	78	210	224
Total	549	797	831	956	1003
Weight percent					
Fibrous Layer	22	14	9	22	22
Contractible elements	0	3	4	4	8
Resin	78	83	87	74	70
Fiber concentration, g/cm ³	0.20	0.11	0.07	0.15	0.18
Total thickness, mm	0.6	1.0	1.1	1.4	1.5
Loop base, B, mm	Na	2.8	2.4	1.87	1.42
Loop H/B ratio	Na	0.36	0.45	0.76	1.07
Gather					
Over-feed ratio	Na	1.0	1.36	1.13	1.31
Contraction ratio	1.0	1.0	1.4	2.3	4.2
Total gather	1.0	1.0	1.9	2.6	5.5
Fraction of original area	1.0	1.0	0.52	0.38	0.18
Stretchability, %	0	0	0	0	0
Abrasion resistance					
Test duration, 10 ³ cycles	4	12	15	15	15
Wear, mm/10 ³ cycles	0.033	0.034	0.015	0.007	0.003
% normalized wear*	100	100	45	21	10
Notes: * % normalized wear is normalized to Sample J					

5 "Na" means not applicable

Example 5

This example illustrates the deleterious effects of excessive stretchability on the abrasion resistance of resin-impregnated contracted fabrics. Three pairs of samples, (10 and 11), (12 and M) and (N and O), were prepared by the procedures of Example 1, Sample 2. The starting fibrous layer of Kevlar[®] aramid fiber of each sample was stitchbonded with about 25% over-feed to provide samples with differing amounts of total gather. The stitch bonded layers were then resin-impregnated with the same polyurethane resin as in Example 1, with the resin amounting to a much lower percent of the total weight of the resin-impregnated sample; namely, about 6 to 33 percent versus about 57 to 87% in Example 1. The lesser amounts of resin were applied to the fibrous layer by dipping the layer a

- "ZAR" polyurethane resin solution that had been diluted with an organic solvent. Details of sample construction and results of abrasion testing are summarized in Table V, below. When the resin in the sample amounted to less than about 20% of the total sample weight, the sample was excessively stretchable. To assure that at least one sample in each pair was dimensionally stable and substantially non-stretchable, inelastic strips were adhesively attached to the back of Samples 10, 12 and 13, but not to the other member of the pair (i.e., samples 11, M and O).

TABLE V

Sample Identification	<u>10</u>	<u>11</u>	<u>12</u>	<u>M</u>	<u>13</u>	<u>N</u>
Unit weight, g/m ²						
Fibrous Layer	166	166	227	227	197	197
Total	509	509	400	400	302	302
Weight percent						
Fibrous Layer	47.0	47.0	56.8	56.8	65.2	65.2
Contractible elements	20.3	20.3	24.6	24.6	28.1	28.1
Resin	32.7	32.7	18.6	18.6	6.7	6.7
Fiber concentration, g/cm ³	0.10	0.10	0.13	0.13	0.15	0.15
Total thickness, mm	1.7	1.7	1.8	1.8	1.3	1.3
Loop base, B, mm	1.1	1.1	1.2	1.2	1.5	1.5
Loop H/B ratio	1.55	1.55	1.45	1.45	1.52	1.52
Gather						
Over-feed ratio	1.25	1.25	1.24	1.24	1.23	1.23
Contraction ratio	4.7	4.7	4.5	4.5	3.9	3.9
Total gather	5.9	5.9	5.6	5.6	4.8	4.8
Fraction of original area	0.17	0.17	0.18	0.18	0.21	0.21
Stretchability, %	0	10	0	70	0	100
Abrasion resistance						
Test duration, 10 ³ cycles	20	20	5	2.1	4	0.8
Wear, mm/10 ³ cycles	0.048	0.051	0.071	0.61	0.114	1.30
Relative wear within pair	1.0	1.06	1.0	8.6	1.0	11.4
Relative wear rating*	1.0	1.06	1.47	12.7	2.3	27.1

Notes: Relative wear within pair is relative to the more abrasion-resistant sample and relative wear rating of individual samples is relative to Sample 10.

- The results summarized in Table V show that even with high total gather and high loop H/B ratios within the invention, unless the loops are immobilized by sufficient resin and unless the fabric is dimensionally stable, contracted resin-impregnated fabric has inadequate abrasion resistance. Note that stretchability of 10% in Sample 11 was not deleterious to abrasion resistance. Note also that dimensional stabilization of Samples 12 and N resulted in considerably greater

abrasion resistance than the corresponding samples (M and O respectively) that was not so stabilized. Note however, that the lack of immobilization of the loops in Samples N and O, because of the very low resin content of the samples, also resulted in much poorer abrasion resistance.

- 5 Although the invention was illustrated primarily with fibrous layers of Kevlar[®] aramid staple fibers and of flash-spun continuous plexifilamentary strands of polyethylene film fibrils, which layers were impregnated with polyurethane or rubber resins, other natural or synthetic fibrous materials (e.g., nylon, polyester, rayon, cotton and the like) and other resins (e.g., epoxy, polystyrene, etc.) can be
10 used in accordance with the present invention to the produce abrasion-resistant, resin-impregnated fabrics. The resins can be applied from aqueous solutions as well as solutions of the resin in organic solvents. Also, the resin-impregnated fabrics of the invention are useful, not only as flat sheet-like articles, but as shaped or molded articles as well as. When used in molded products, some of the
15 contraction imposed on the flat fabric is removed by the molding operation. In such cases, the residual amount of contraction in the molded article is very important in determining the abrasion-resistant characteristics of the resin-impregnated article. Resin-impregnated fabric of the invention can be used as a single layer or in multiple superimposed layers or in combination with other
20 gathered fabrics, flat fabrics or sheets and in flat or in shaped form. The fabric can be permanently attached to or molded over articles, such as elbow pads for jackets, back-packs, luggage, shoes, or portions thereof, and the like.

I CLAIM:

1. A process for preparing an abrasion-resistant resin-impregnated nonwoven fabric comprising the steps of:

5 contracting a nonwoven fibrous layer in area to an area that is no greater than one-half its original non-contracted area of the layer and causing groups of fibers of the nonwoven fibrous layer to buckle out of the plane of the layer and form inverted U-shaped loops projecting in a direction generally perpendicular to the plane of the layer,

10 immobilizing the buckled groups of fibers, and stabilizing the dimensions of the contracted fibrous layer.

2. A process in accordance with claim 1 wherein the fibrous layer area is contracted to less than one-third the original area.

3. A process in accordance with claim 1 wherein a contractible element or array of contractible elements is intermittently attached to the nonwoven fibrous layer, the intermittently attached element or array of elements is contracted to cause an accompanying contraction of the nonwoven fibrous layer and the buckling of the groups of fibers.

4. A process in accordance with claim 3 wherein the buckled groups of fibers are immobilized by impregnating the fibrous layer with a resin and then curing and/or drying the resin.

5. A process in accordance with claim 4 wherein the dimensions of the contracted layer are stabilized simultaneously with the immobilization of the buckled groups of fibers during the resin-impregnation-and-curing step.

6. A process in accordance with claim 4 wherein the dry resin amounts to in the range of 10 to 90% of the total weight of the impregnated layer.

7. A process in accordance with claim 6 wherein the dry resin amounts to 25 to 75% of the total weight of the impregnated layer.

8. A resin-impregnated nonwoven fabric comprising a fibrous layer from which groups of fibers are buckled out of plane, the buckled groups of fibers having an average spacing in the range of 0.5 to 3 mm and an average loop height-to-base ratio of at least 0.5, and the fabric being stretchable in any linear direction by no more than 50% and weighing in the range of 150 to 1200 g/m² of which weight 10 to 90 weight percent consists of resin.

9. A fabric of claim 8 where the average spacing of the buckled groups of fibers is in the range of 1 to 2 mm, and the fabric is stretchable by no more than 25%.

10. A fabric of claim 9 wherein the loop height-to-base ratio is in the range of 0.7 to 1.5 and the fabric is stretchable by no more than 5%.

FIG. 1

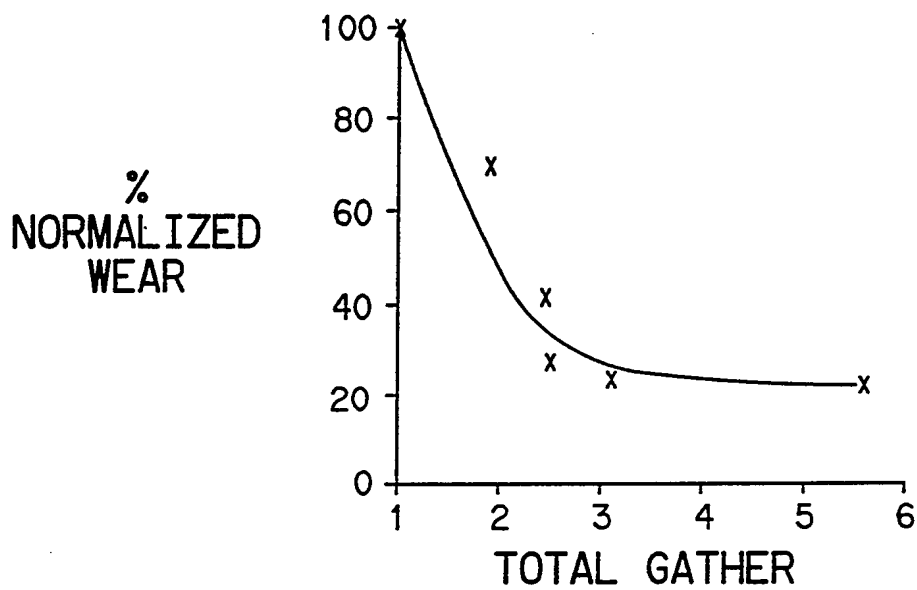


FIG. 2

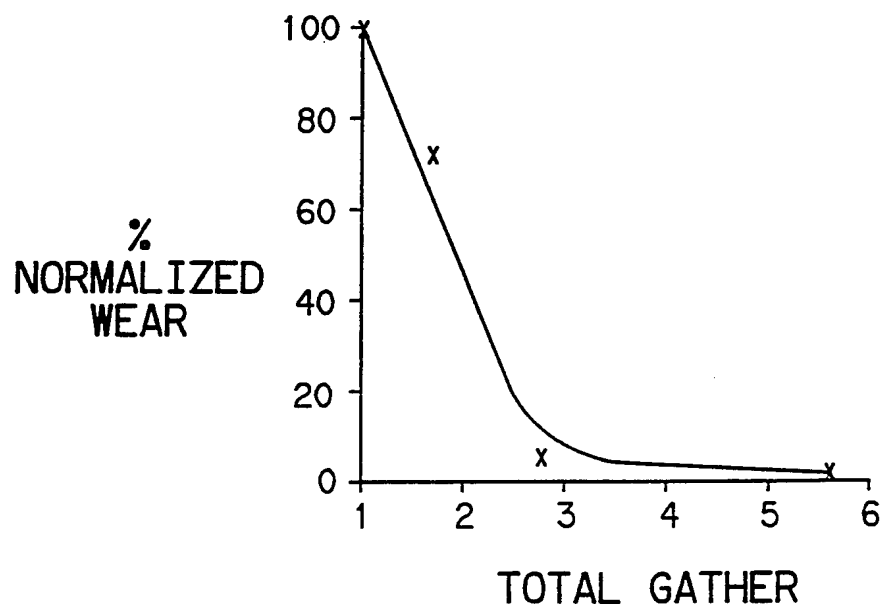


FIG.3

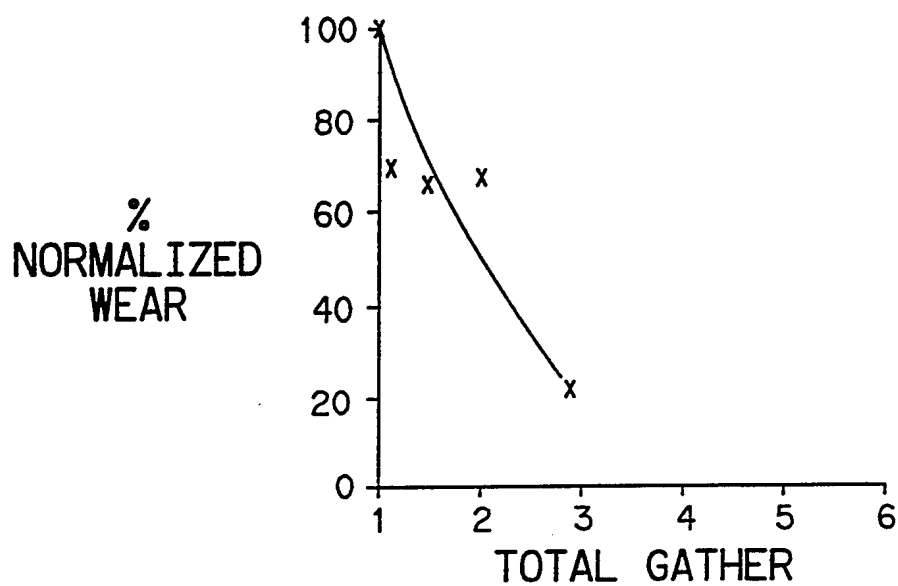


FIG.4

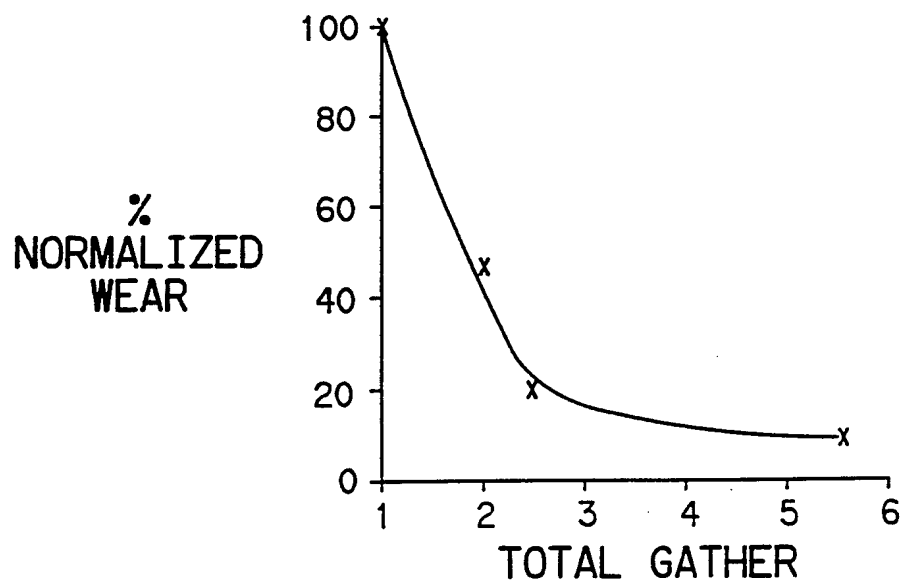


FIG. 5

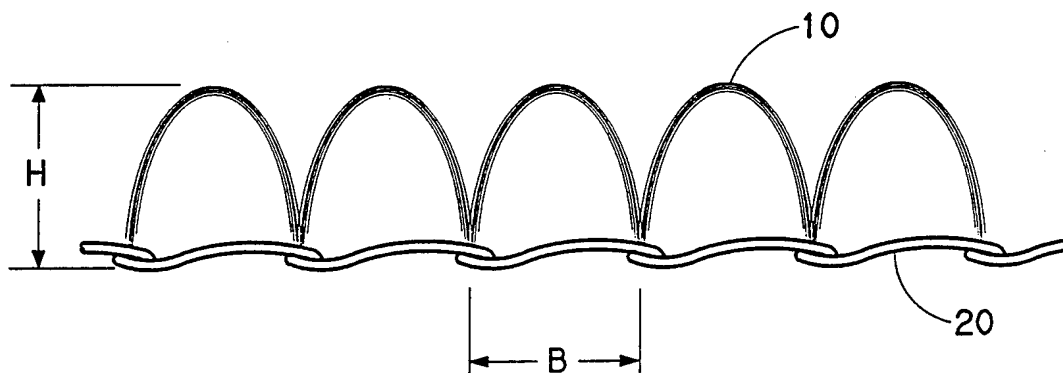
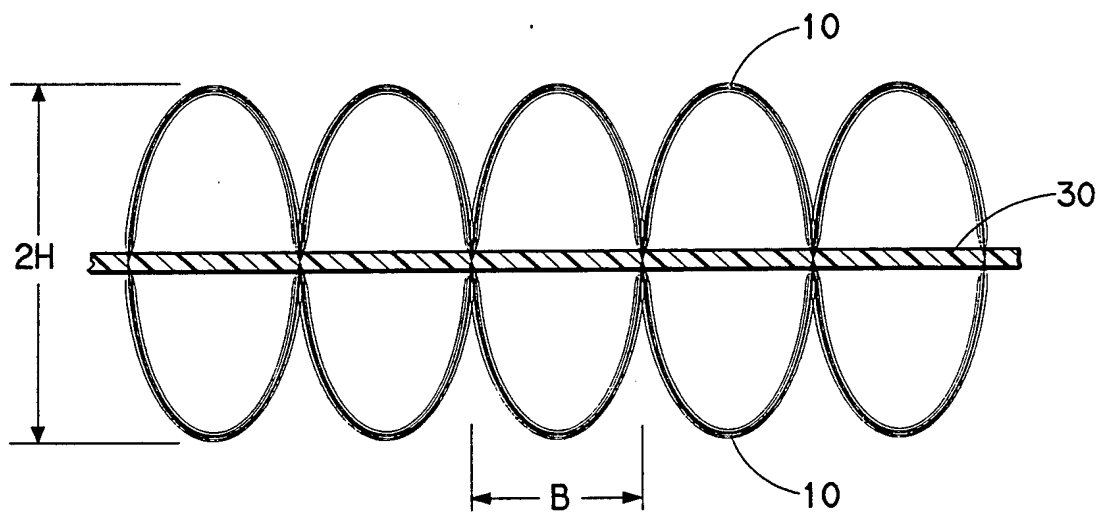


FIG. 6



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 94/01481

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 D04H1/74

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 D04H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,3 709 764 (GORDON D. THOMAS) 9 January 1973	1-4
A	see the whole document ---	6-10
X	DATABASE WPI Section Ch, Week 9107, Derwent Publications Ltd., London, GB; Class A84, AN 91047905 & JP,A,3 000 035 (KANAI) 27 May 1989 see abstract ---	1
X	DATABASE WPI Section Ch, Week 7918, Derwent Publications Ltd., London, GB; Class A94, AN 7934614 & JP,A,54 007 996 (HIROYUKI) 11 April 1979 see abstract ---	1-3
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

2 June 1994

Date of mailing of the international search report

17. 06. 94

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 94/01481

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 2892, Derwent Publications Ltd., London, GB; Class A28, AN 92228521 & JP,A,4 146 082 (KANAI) 20 May 1992 see abstract ---</p>	1-5
A	<p>US,A,3 404 062 (DONALD FLOYD MILLER) 1 October 1968 see the whole document ---</p>	1-10
A	<p>US,A,3 468 748 (ALTON H. BASSET) 23 September 1969 cited in the application see claims ---</p>	1-4
A	<p>US,A,4 606 964 (RONALD H. WIDEMAN) 19 August 1986 cited in the application see claims -----</p>	1-10

INTERNATIONAL SEARCH REPORT

information on patent family members

International application No.

PCT/US 94/01481

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US-A-3404062		NONE	
US-A-3468748	23-09-69	NONE	
US-A-4606964	19-08-86	NONE	